

Letters

Enrichment of Deuterium Oxide at Hydrophilic Interfaces in Aqueous Solutions

Johan J. R. Stålgren,[†] Katrin Boschkova,[‡] Jan-Christer Ericsson,[§] Curtis W. Frank,[†]
Wolfgang Knoll,^{||} Sushil Satija,[⊥] and Michael F. Toney^{*,‡}

Department of Chemical Engineering, Stanford University, Stanford, California 94305, Institute for Surface Chemistry, Box 5607, SE-114 86 Stockholm, Sweden, Department of Chemistry, Surface Chemistry, Royal Institute of Technology, Box 5607, SE-100 44 Stockholm, Sweden, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany, NIST Center for Neutron Scattering, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Menlo Park, California 94025

Received March 31, 2007. In Final Form: September 7, 2007

The structure of water at aqueous interfaces is of the utmost importance in biology, chemistry, and geology. We use neutron reflectivity and quartz crystal microbalance to probe an interface between hydrophilic quartz and bulk liquid solutions of H₂O/D₂O mixtures. We find that near the interface the neutron scattering length density is larger than in the bulk solution and there is an excess adsorbed mass. We interpret this as showing that there is a region adjacent to the quartz that is enriched in D₂O and extends 5–10 nm into the solution. This suggests caution when interpreting results where D₂O is substituted for H₂O in aqueous interfacial chemistry.

Water is complex with unusual properties resulting from its small size and strongly polar hydrogen bonds.¹ Due to the importance of aqueous interfaces in a variety of fields and to their common occurrence in nature,² much work has been directed toward understanding solid–liquid interfaces. Theoretical investigations on water next to hydrophilic (attractive) interfaces, including molecular dynamics and Monte Carlo simulations, have been performed.^{3–10} These show that water forms molecular layers next to hydrophilic (attractive) interfaces that extend a

few molecular diameters from the interface; density profiles and the orientation of the interfacial water molecules have been calculated. It has been suggested that the layering induces additional structuring in water extending more (possibly much more) than a few molecular diameters from the interface.¹¹ This, however, remains controversial¹² and is under active investigation. Several experimental surface techniques have been used to probe aqueous interfaces at a molecular level including X-ray and neutron scattering, surface forces measurements, and optical

* To whom correspondence should be addressed. E-mail: mftoney@slac.stanford.edu.

[†] Stanford University.

[‡] Institute for Surface Chemistry.

[§] Royal Institute of Technology.

^{||} Max Planck Institute for Polymer Research.

[⊥] National Institute of Standards and Technology.

[‡] Stanford Linear Accelerator Center.

(1) Franks, F. *Water: A Comprehensive Treatise*; Plenum: New York, 1972–82; Vol. 1–7.

(2) Allara, D. L. *Nature* **2005**, 437, 638–639.

(3) Guidelli, R.; Schmickler, W. *Electrochim. Acta* **2000**, 45, 2317–2338.

(4) Hayashi, T.; Pertsin, A. J.; Grunze, M. *J. Chem. Phys.* **2002**, 117, 6271–6280.

(5) Pertsin, A. J.; Grunze, M. *J. Chem. Phys.* **2003**, 118, 8004–8009.

(6) Forsman, J.; Woodward, C. E.; Jonsson, B. *Langmuir* **1997**, 13, 5459–5464.

(7) Lee, S. H.; Rossky, P. J. *J. Chem. Phys.* **1994**, 100, 3334.

(8) Lu, L.; Berkowitz, M. L. *Mol. Phys.* **2006**, 104, 3607–3617.

(9) Hirunsit, P.; Balbuena, P. B. *J. Phys. Chem. C* **2007**, 111, 1709–1715.

(10) Besseling, N. A. M. *Langmuir* **1997**, 13, 2113–2122.

(11) Zheng, J.-m.; Chin, W.-C.; Khijniak, E.; Khijniak, J. E.; Pollack, G. H. *Adv. Colloid Interface Sci.* **2006**, 127, 19–27.

(12) Israelachvili, J.; Wennerstrom, H. *Nature* **1996**, 379, 219–225.

techniques such as second-harmonic generation¹³ and sum-frequency generation.^{14,15} The vibrational spectra from the water–surface interactions show characteristics indicating that the interfacial water molecules form a hydrogen-bonding network more ordered than the bulk water (i.e., ice-like). A recent investigation utilizing the phase-sensitive sum-frequency vibrational spectroscopic technique identified both liquid-like (disordered) and ice-like (ordered) water components in contact with hydrophilic quartz depending on pH.¹⁵ X-ray scattering has been used to study water in contact with metal, oxide, and salt interfaces,^{16–20} where the presence of one or more interfacial molecular layers has been observed as well as has the effect of the substrate structure on the interfacial water. Surface force measurements¹² show layering extending 1–2 nm from aqueous–solid interfaces. Thus, while much is known about the arrangement of water at hydrophilic aqueous–solid interfaces, the extent of the influence of the interface is still under debate.

The goal of this work is to investigate the properties of interfacial water at hydrophilic SiO₂ interfaces in H₂O/D₂O mixtures. There are small but distinct differences in physical properties between H₂O and D₂O liquids with D₂O having more structural order, which is due to the slightly (~5–10%) stronger hydrogen bond in D₂O compared to H₂O.^{21,22} However, there are no expectations that the interface structure of H₂O and D₂O will differ significantly. We use both neutron reflectivity and quartz crystal microbalance (QCM) to show that, at the interface between hydrophilic SiO₂ and a liquid bulk solution of H₂O/D₂O mixtures, there is a region adjacent to the SiO₂ that is different from the bulk solution and extends 5–10 nm into the solution. We interpret our data as showing that there is a preferential enrichment of D₂O at this interface. The combination of these two experimental probes provides evidence for this enrichment and suggests caution when interpreting results where D₂O is isotopically substituted for H₂O in aqueous interfacial chemistry. Previous neutron reflectivity experiments on H₂O/D₂O mixtures in contact with quartz²³ saw evidence for a similar enhancement, but these were for high concentrations of D₂O (60–100%) and were interpreted as evidence for protonic quantum entanglement²⁴ or some unexplained physical chemistry of isotope mixtures.

For this investigation we have chosen two different in-situ techniques: neutron reflectivity^{25–27} and QCM.^{28,29} Both tech-

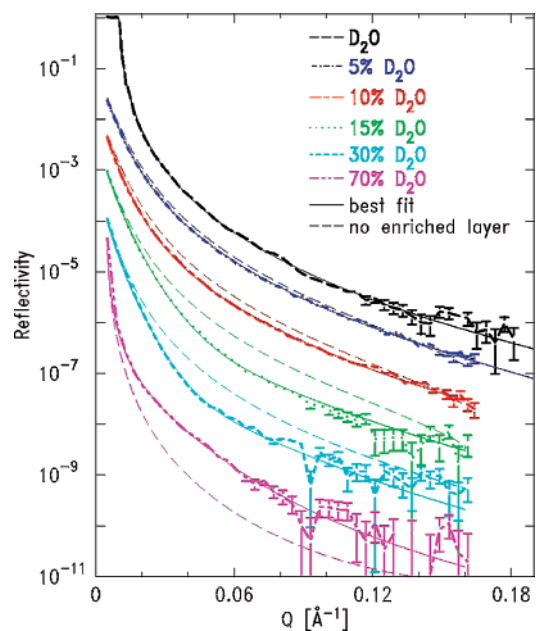


Figure 1. Measured (thick lines) and fitted neutron reflectivity for the quartz–H₂O/D₂O mixtures. The thin solid lines show the best fits with an interfacial region adjacent to the interface that has a scattering length density larger than the bulk H₂O/D₂O mixture, while the fits without this interfacial layer are the thin, dashed lines. Data are offset for clarity.

niques are sensitive to the mass of liquid molecules perpendicular to a solid–liquid interface, but they probe fundamentally different physical properties. Details of the experiments and data modeling can be found in the Supporting Information. The reflectivity data were analyzed using the Parratt formalism^{25–27} with an interfacial layer with a uniform neutron scattering length density next to the interface and an exponential decay into the solution. The data are not sensitive to either the shape of this decay or to the decay length; thus, in some of the fits to the data the decay length and interfacial width fitting parameters were held fixed (since these tended to diverge). More details are found in the Supporting Information.

Specular neutron reflectivity is used to measure the distribution of D₂O and H₂O adjacent to the hydrophilic quartz interface. Because the scattering length densities of D₂O and H₂O are different (6.33×10^{-6} and $-0.56 \times 10^{-6} \text{ Å}^{-2}$, respectively),^{26,27,30} neutron reflectivity is able to distinguish these species. Figure 1 (heavy lines) shows the neutron reflectivity from D₂O and H₂O/D₂O mixtures, which are analyzed using a model based on the Parratt formalism.^{25–27} The model includes surface roughness at the quartz–solution interface and an interfacial layer with a uniform scattering length density next to the interface and an exponential tail, as shown in Figure 2. To improve the reliability of the models for H₂O/D₂O mixtures, data for pure D₂O are used to determine the neutron scattering length density of the quartz substrate and data for quartz–air and quartz–D₂O determine the quartz roughness ($0.43 \pm 0.02 \text{ nm}$, which is consistent with previous results^{31,32}). These values are fixed for modeling the mixture data.

The best-fit best models of the data with no interfacial layer are shown by the thin dashed line in Figure 1. Here there is a

- (13) Vidal, F.; Tadjeddine, A. *Rep. Prog. Phys.* **2005**, *68*, 1095–1127.
- (14) Richmond, G. L. *Chem. Rev.* **2002**, *102*, 2693–2724.
- (15) Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. *Phys. Rev. Lett.* **2005**, *94*, 046102.
- (16) Cheng, L.; Fenter, P.; Nagy, K. L.; Schlegel, M. L.; Sturchio, N. C. *Phys. Rev. Lett.* **2001**, *87*, 8715.
- (17) Toney, M. F.; Howard, J. N.; Richer, J.; Borges, G. L.; Gordon, J. G.; Melroy, O. R.; Wiesler, D. G.; Yee, D.; Sorensen, L. B. *Nature* **1994**, *368*, 444–446.
- (18) Arsic, J.; Kaminski, D. M.; Radenovic, N.; Poodt, P.; Graswinckel, W. S.; Cuppen, H. M.; Vlieg, E. *J. Chem. Phys.* **2004**, *120*, 9720–9724.
- (19) Eng, P. J.; Trainor, T. P.; Brown, G. E., Jr.; Waychunas, G. A.; Newville, M.; Sutton, S. R.; Rivers, M. L. *Science* **2000**, *288*, 1029–1033.
- (20) Chu, Y. S.; Lister, T. E.; Cullen, W. G.; You, H.; Nagy, Z. *Phys. Rev. Lett.* **2001**, *86*, 3364.
- (21) Dore, J. C.; Garawi, M.; Bellissent-Funel, M. C. *Mol. Phys.* **2004**, *102*, 2015–2035.
- (22) Devlin, J. P. *J. Chem. Phys.* **2000**, *112*.
- (23) Abdul-Redah, T.; Daub, C.; Streffer, F.; Chatzidimitriou-Dreismann, C. A. *Physica B* **2000**, *291*, 314–316.
- (24) Chatzidimitriou-Dreismann, C. A.; Abdul-Redah, T.; Streffer, R. M. F.; Mayers, J. *Phys. Rev. Lett.* **1997**, *79*, 2839–2842.
- (25) Dura, J. A.; Richter, C. A.; Majkrzak, C. F.; Nguyen, N. V. *Appl. Phys. Lett.* **1998**, *73*, 2131–2133.
- (26) Lu, J. R.; Thomas, R. K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 995–1018.
- (27) Fragneto, G.; Lu, J. R.; McDermott, D. C.; Thomas, R. K.; Rennie, A. R.; Gallagher, P. D.; Satija, S. K. *Langmuir* **1996**, *12*, 477–486.
- (28) Rodahl, M.; Hook, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. *Rev. Sci. Instrum.* **1995**, *66*, 3924–3930.
- (29) Rodahl, M.; Kasemo, B. *Rev. Sci. Instrum.* **1996**, *67*, 3238–3241.

- (30) Schwendel, D.; Hayashi, T.; Dahint, R.; Pertsin, A.; Grunze, M.; Steitz, R.; Schreiber, F. *Langmuir* **2003**, *19*, 2284–2293.
- (31) Forciniti, D.; Hamilton, W. A. *J. Colloid Interface Sci.* **2005**, *285*, 458–468.
- (32) Burgess, I.; Li, M.; Horswell, S. L.; Szymanski, G.; Lipkowski, J.; Majewski, J.; Satija, S. *Biophys. J.* **2004**, *86*, 1763–1776.

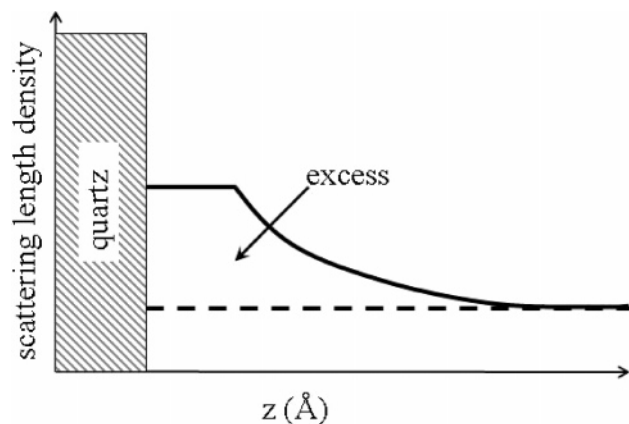


Figure 2. Schematic profile of neutron scattering length density adjacent to the quartz surface. We interpret the larger scattering length density near the interface as an enrichment in D_2O concentration. The surface excess of D_2O is indicated.

uniform scattering length density that is the same as the bulk solution up to the quartz surface. As is apparent, the neutron reflectivity for the H_2O/D_2O mixtures is significantly different from that expected for no interfacial layer. This result agrees with a similar neutron reflectivity experiment on clean quartz in contact with H_2O/D_2O mixtures of 60–100% D_2O .²³ These data could also only be fitted with an additional interface layer with scattering length density higher than the bulk solution, which was reported to be physically fictitious, and the measurements were interpreted as evidence for protonic quantum entanglement²⁴ (although this has been disputed³³) or some unexplained physical chemistry of isotope mixtures. We have also modeled our reflectivity data with an interfacial region adjacent to the surface that has a scattering length density larger (more positive) than the bulk H_2O/D_2O mixture. The best fits to the data are shown by the thin, solid lines in Figure 1, which show that this model reproduces the interfacial system significantly better than the no-interfacial layer (thin dashed lines). For pure D_2O , there is a slight increase in the scattering length density at the interface (102% of bulk solution scattering length density, consistent with neutron reflectivity measurements on hydrophilic self-assembled monolayers in contact with D_2O ³⁰). This increase is just outside the error bars and could result from a small increase in density near the interface. The data and analysis for pure H_2O are much less sensitive to the interfacial region due to the weaker reflectivity and the higher background. We have checked the possibility that adventitiously adsorbed hydrocarbons could cause the observed reflectivity and find that a thin (0.5–1 nm) hydrocarbon layer cannot model our data (see Supporting Information, Figure S1).

Figure 3 shows the neutron scattering length densities from the best fits to the mixture data shown by the thin solid lines in Figure 1, and the best-fit fitting parameters are tabulated in Table S1. There is an increase in the scattering length densities adjacent to the quartz surface (at $z = 0$) and this region extends perpendicular to the hydrophilic surface by 5–10 nm before decaying to bulk solution values. The extent and exact shape of this region cannot be accurately determined (error bars of about 2–4 nm) because of the diffuse nature of this region and the Q range available in neutron reflectivity. Despite this inaccuracy, there appears to be a decrease in the extent of this region of enhanced scattering length density (from about 12 nm to about 4 nm) with increasing bulk D_2O , as shown in Figure 3 and Table S1. However, more work is needed to confirm this. To verify

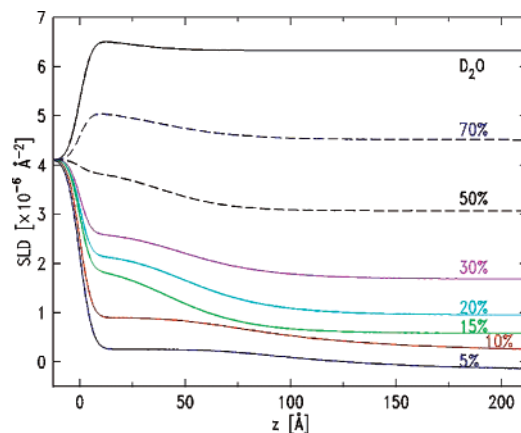


Figure 3. Neutron scattering length densities (SLDs) as a function of distance above the quartz surface (defined as $z = 0$).

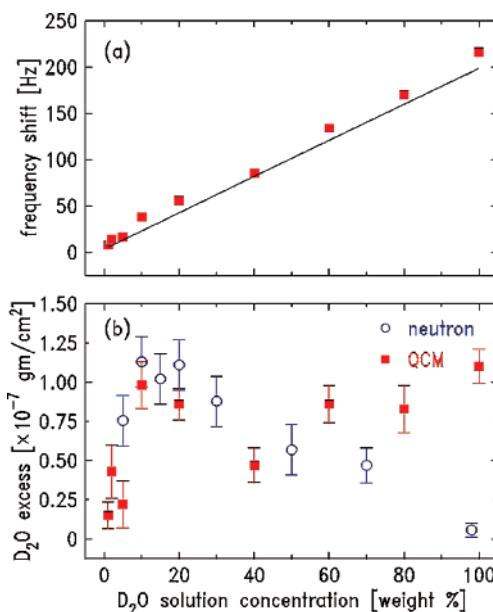


Figure 4. (a) Frequency shifts from the QCM (filled red squares). Error bars are less than the size of the data points. The solid line is the theoretical model including the effect of interfacial roughness trapping water. A model without roughness is only slightly different from this (about 4 Hz less). The D_2O concentration was increased by continuously exchanging the solution in the measurement cell with a solution with more D_2O . (b) Dependence of the surface excess on D_2O bulk solution concentration as calculated from neutron reflectivity (open blue circles) and QCM (filled red squares).

our results, we conducted independent neutron reflectivity measurements with H_2O/D_2O mixtures at an oxidized Si substrate (40 nm SiO_2 on Si) and obtained results quantitatively consistent with those reported here.

The QCM is an acoustic device that has high sensitivity to changes in areal mass density at its surface (solid–liquid interface, in our case). Figure 4a shows the QCM frequency shift (where zero is for pure H_2O) for different concentrations of H_2O/D_2O mixtures. Here the D_2O concentration is slowly increased from pure H_2O to pure D_2O . The solid line in Figure 4a shows the behavior expected from theory³⁴ accounting for the density and viscosity increase from H_2O to D_2O (assuming bulk values) and the effect of interfacial roughness.³⁵ The observed frequency is systematically higher than that expected from theory. However,

(33) Ioffe, A.; Arif, M.; Jacobson, D. L.; Mezei, F. *Phys. Rev. Lett.* **1999**, *82*, 2322–2325.

(34) Kanazawa, K. K.; Gordon, J. G. *Anal. Chim. Acta* **1985**, *175*, 99–105.
(35) Martin, S. J.; Frye, G. C.; Wessendorf, K. O. *Sens. Actuators A* **1994**, *44*, 209–218.

the QCM dissipation (a measure of energy loss) follows theory to better than 1% (not shown). These observations, taken together, show the presence of an excess adsorbed mass at the interface. Control experiments were performed with 100% D₂O and 100% H₂O on a hydrophobic thiohexadecane (CH₃(CH₂)₁₅SH) surface. Both the frequency and dissipation followed theory within 1–2% without any indication of excess areal mass density. These results rule out the possibility of contamination creating an artificial interfacial excess adsorbed mass.

We interpret both the QCM and neutron reflectivity results to show that there is a region adjacent to the surface that has an enhanced concentration of D₂O (see Figure 2). This interpretation explains both the excess interfacial adsorbed mass from the QCM and the increase in the scattering length densities adjacent to the quartz in the neutron reflectivity. One test of this interpretation is to quantitatively compare the QCM and reflectivity results. We have done this by using the neutron results (Figure 3), assuming that the excess neutron scattering length density is due to an enrichment in D₂O, and then calculating the surface excess D₂O, which is the integral of the excess interfacial D₂O, as shown in Figure 2. This is converted into an equivalent areal mass density of D₂O (g/cm²) assuming this layer is pure D₂O (density of 1.1 g/cm³). This surface excess is shown in Figure 4b and compared with the QCM results where the excess frequency shift (above the theory line in Figure 4a) is converted into areal mass density.³⁶ Considering that the QCM and neutron reflectivity probe fundamentally different physical properties, the agreement in Figure 4b is remarkable and strongly supports our conclusions. The apparent disagreement between the QCM and reflectivity of pure D₂O is likely due to changes in the properties of the interface that are not accounted for in the current QCM theory (e.g., viscosity or density).

Although it is possible that our results could be caused by an interfacial layer with the same concentration as the bulk solution (i.e., not enriched in D₂O) but with a significantly higher mass density, we think this is unlikely. First, this cannot explain the 5% D₂O data, where the neutron scattering length density in the interfacial layer has the opposite sign (positive) as that of the bulk solution (negative). Second, if there is a higher density layer, then this larger density should be evident in the pure solutions, but we only observe a small increase in interfacial density (2%). Third, the density of this hypothetical high-density layer would have to vary with D₂O concentration from 2 to 3 g/cm³ at 10–20% D₂O to 1.2 g/cm³ at 70% D₂O, which seems unlikely.

Our results show that there is a layer at the hydrophilic quartz–aqueous (H₂O/D₂O) interface that is enriched in D₂O and extends into the solution a surprisingly large distance, ~5–10 nm (Figure

3). This suggests that the liquid layers immediately adjacent to the quartz interface are different in H₂O and D₂O, which could be tested with interface sensitive optical methods.¹⁵ The D₂O excess shown in Figure 4b increases rapidly up to about 10 wt % D₂O in the bulk solution and then saturates at about 1×10^{-7} g/cm² (equivalent to about 1 nm of D₂O) before slowly decreasing. Hence, the major mechanism causing the D₂O enrichment occurs at a low (10%) bulk D₂O concentration. While the mechanism causing this preferential D₂O enrichment is unclear, we offer two possible explanations. First, the arrangement of water molecules in the interfacial layer could be different from bulk water, which could drive the D₂O interfacial segregation. The extent of this region would be significantly larger than the few nanometers (several molecular diameters) that are predicted by modeling.^{3,4,6–8} Second, we note that some models of bulk water invoke a clustering of molecules to explain the properties of water.^{37,38} Given that hydrogen bonding in D₂O is stronger than in H₂O,^{21,22} it is plausible that D₂O clusters would be more stable than H₂O clusters. If such clusters are integral to the interfacial layer, then the increased stability of D₂O clusters provides a possible mechanism for the D₂O enrichment.

Finally, D₂O is often substituted for H₂O with the implicit assumption that the physical chemistry is unchanged. For example, this approach is used in neutron scattering to achieve favorable contrast in scattering length density.^{26,27,30} Our results suggest that this approach should be used cautiously in experiments involving interfaces, and possibly bulk solutions, as it can lead to artifacts in data analysis and interpretation. This agrees with Dore et al.,²¹ who suggest that, based on the distinguishable characteristics of D₂O and H₂O, H/D substitution is not a true isomorphic replacement.

Acknowledgment. We thank Y. S. Seo for experimental assistance with the neutron reflectivity. J.J.R.S. acknowledges financial support from CPIMA (Center on Polymer and Interfacial Macromolecular Assemblies), the Wenner-Gren Foundation and Q-Sense AB. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

Supporting Information Available: Details of the experiments, the data modeling (with a table of the fitting parameters), and a comparison that shows our results are not due to hydrocarbon contamination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA700932S

(36) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206–222.

(37) Chaplin, M. F. *Biophys. Chem.* **2000**, *83*, 211–221.

(38) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808–1827.